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COMBUSTION TRIALS WITH SYNCRUDE COKE IN A PILOT-SCALE ATMOSPHERIC BUBBLING FLUIDIZED BED

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COMBUSTION TRIALS WITH SYNCRUDE COKE IN A PILOT-SCALE ATMOSPHERIC BUBBLING FLUIDIZED BED

by

E.J. Anthony*, D.L. Desai** and F.D. Friedrich*

ABSTRACT

Syncrude coke is a fluid coke produced in the upgrading of bitumen derived from oil sands. As a fuel it is high in sulphur, low in volatiles, and relatively unreactive, a combination which makes it intractable to conventional combustion technology, although good performance has been demonstrated in circulating fluidized bed combustors.

The present work demonstrates that due to the fine size consist of the coke, and the consequent elutriation, it is difficult to achieve good combustion efficiency in a bubbling fluidized bed combustor. Even under the favourable conditions of a low fluidizing velocity (1 m/s) and a high inventory of "fines" in the bed material, carbon combustion efficiency ranged between 56 and 74%. Fort McMurray limestone appears to be a satisfactory sulphur sorbent, although the relationship between Ca/S ratio and sulphur capture could not be accurately quantified because a large portion of the sulphur remained fixed with the unburned carbon. NO_x emissions were generally within the national guidelines of 258 ng/J.

Combustion efficiency could probably be improved by pretreating the fuel to obtain a coarser size consist. However, it is concluded that a bubbling bed combustor, because of the higher limestone requirement and the large bed area required to achieve a low fluidizing velocity, would be uncompetitive with a circulating bed combustor.

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ESSAIS DE COMBUSTION AVEC DU COKE DE BRUT SYNTHÉTIQUE DANS UNE CHAMBRE À COMBUSTION AVEC LIT FLUIDISÉ À BULLES À LA PRESSION ATMOSPHÉRIQUE À L'ÉCHELLE-PILOTE

par

E.J. Anthony*, D.L. Desai** et F.D. Friedrich*

RÉSUMÉ

Le coke de brut synthétique est un coke fluide produit lors de l'amélioration du bitume provenant des sables pétrolifères. En tant que combustible, ce coke a une haute teneur en soufre, une faible teneur en matières volatiles et il est relativement inerte. Cette combinaison de caractéristiques le rend intraitable avec les techniques de combustion classiques, même si on a réussi à obtenir un bon rendement lors des essais dans des chambres à combustion à lit fluidisé circulant.

Les résultats des présents travaux de recherche démontrent qu'en raison de la fine répartion granulométrique du coke et par la suite l'élutriation qui en résulte, il est difficile d'atteindre un bon rendement de combustion dans une installation à combustion à lit fluidisé à bulles. Même dans des conditions favorables c'est-à-dire à faible vitesse de fluidisation (1 m/s) et avec une quantité élevée de "fines" dans le matériau du lit, le rendement de combustion du carbone se situait entre 56 et 74 %. Le rendement du calcaire de Fort McMurray comme sorbant du soufre semblait toutefois satisfaisant, malgré que la relation entre le rapport Ca/S et la capture du soufre ne pouvait être quantifiée en raison des quantités élevées de soufre demeurées fixées au carbone non brûlé. Les émissions de NO_x, en général, ne dépassaient pas les normes canadiennes admises de 258 ng/J.

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Le rendement de combustion pourrait être amélioré à l'aide d'un procédé de prétraitement du combustible qui permettrait d'obtenir une répartition granulométrique grossière. Toutefois, il est possible de conclure qu'une installation de combustion à lit fluidisé à bulles ne peut concurrencer une installation de combustion à lit fluidisé circulant en raison des besoins élevés en calcaire du lit à bulles et de la grande dimension de lit nécessaire pour obtenir d'une faible vitesse de fluidisation.

INTRODUCTION

Canada's largest oil sands extraction plant located in Fort McMurray, Alberta and operated by Syncrude Canada Ltd. produces about 2000 t/d of fluid coke as a byproduct of its bitumen upgrading process. The coke is high in sulphur, low in volatiles, relatively unreactive, and has a high vanadium content. All these characteristics render it unsuitable for combustion by conventional technology. However, the coke is fairly consistent in quality, and comparable in composition to other petroleum cokes made by fluid coking. Its higher heating value of about 30 MJ/kg makes it an attractive fuel if appropriate combustion efficiencies and sulphur capture can be achieved.

Pilot-scale combustion tests sponsored by CANMET have demonstrated that with circulating fluidized bed combustion (CFBC) technology, Syncrude coke can be burned at a carbon combustion efficiency of about 99%, with 90% sulphur capture (1,2). It was recognized that it would be difficult to achieve comparable results with a bubbling fluidized bed combustor (BFBC) because of high elutriation rates resulting from the fine size consist of the coke. However, for some applications BFBC boilers can be built at lower capital cost than CFBC boilers. Therefore, it seemed advisable to explore the combustion performance of Syncrude coke in a BFBC with Fort McMurray limestone as the sulphur sorbent. This was done in a brief series of tests using CANMET facilities.

FUEL AND LIMESTONE CHARACTERISTICS

The chemical analysis and size distribution of the coke are given in Table 1. It should be noted that the surface mean size is 150 μm, and typically 98% of the material is <0.5 mm while 67% is <0.25 mm. It is this property which results in excessive fuel elutriation in BFBC systems operating with superficial fluidizing velocities above 1 m/s.

The limestone which was used is known alternatively as Fort McMurray or more properly as Athabasca limestone. It contains approximately 75% $CaCO_3$, and its analysis is given in Table 2. Bench-scale reactivity tests have shown it to be only a moderately good sulphur sorbent at the size ranges appropriate to BFBC, but geography dictates that it would be used if Syncrude coke were burnt at Fort McMurray on an industrial scale. Pilot and bench-scale research

have indicated that this would not pose a problem in CFBC operation as limestone performance improves with decreasing particle size or increasing surface-to-volume ratio (2,3,4).

PILOT-SCALE AFBC

The apparatus is shown schematically in Fig. 1 and has been described in detail in a separate report (5). It consists of a fuel hopper capable of holding approximately 300 kg of solid fuel, a sorbent hopper capable of holding 200 kg of limestone, the combustor, and a multicyclone with a reinjection facility to improve combustion efficiency and sulphur capture.

The combustor is 4.8 m high and has external dimensions of 0.94 x 0.97 m. The internal dimensions are 380 x 406 mm giving a bed area of 0.155 m^2. The bed, which is lined with firebricks and insulating refractory bricks, is instrumented with thermocouples and pressure probes. In addition, there are two inserts on opposite faces of the bed to allow water-cooled tubes to pass through the bed. Although there is a facility for up to 48 in-bed cooling tubes, in practice no more than four were used because of the low fluidizing velocities hence the low thermal input (86-180 kW or approximately 0.3×10^6 to 0.6×10^6 Btu/h).

The air distributor consists of a 9.5 mm thick mild steel plate fitted with 100 bubble caps to allow even distribution of the fluidizing air. The bubble caps are made of 32 x 13 mm diam stainless steel bolts arranged in a 35 x 38 mm rectangular pitch. These bolts are drilled with a 6 mm diam hole through their central axis and four horizontal holes, 3 mm diam, just below the head of the bolt. This arrangement prevents "weeping" and causes air to egress horizontally. A 20-mm gap between the distributor plate and the bolt provides a dead layer of sand which thermally insulates the distributor plate.

The fuel and limestone feed systems consist of a coal hopper and a limestone hopper, each with a variable speed delivery screw connected via a flexible fibreglass hose to a 67 mm diam water-cooled feed screw which delivers the fuel and limestone directly into the bed, 114 mm above the distributor plate. The hoppers sit on electronic weigh scales which permit feed rates to be calculated from the change of weight per unit time. In-bed feeding was used throughout this work to maximize combustion efficiency.

The multicyclone is connected to the freeboard via a "flexible" stainless steel duct. The cyclone products may be either collected in a drum for "non-recycle tests" or pneumatically reinjected back into the bed during tests with fly ash recycle.

Light-up of the combustor is accomplished by using an in-bed propane burner to heat the combustor to near the desired operating temperatures. Solid fuel feed is then initiated, and when stable combustion conditions have been achieved, the propane burner is turned off. Sand is normally used as the starting bed material. In tests involving sulphur capture, limestone feed is initiated concurrently with the solid fuel feed.

The instrumentation is standard and consists of NDIR analyzers to continuously measure CO, CO_2 and SO_2; a UV analyzer for SO_2 (to provide a double check for this important measurement); a paramagnetic analyzer for O_2; and a chemiluminescent NO_x analyzer. The temperatures in the bed, freeboard and cooling circuits are measured by "K-type" thermocouples, and the pressure drop across the bed is measured both by means of a manometer (for quick visual check on the bed height) and by a scanning valve connected to a pressure transducer. All the data are taken to an automatic data acquisition/control system and finally stored on floppy disc every 5 min by a desk-top computer. An electronic data logger also records all the data every 5 min as a backup system.

TEST PROGRAM

As earlier work had indicated that successful operation could not be achieved at velocities higher than 2 m/s, it was decided to attempt one test at a nominal velocity of 1.5 m/s. This was to be initially supported by use of the propane "light-up" burner if necessary. In fact it was found essential to use propane throughout to maintain stable operation even at this low fluidizing velocity. It was therefore decided to conduct the test program at velocities of 1 m/s or less. As sulphur capture was an important parameter, a nominal bed temperature of 850°C was selected. No constraints were set for excess air because of the extremely limited choice of fluidizing velocities. However, it was decided to determine the effect of fly ash recycle on combustion efficiency.

In all, seven combustion runs were carried out. Three of these (BSC-1, BSC-2 and BSC-3) were baseline tests in which fuel feed rate was

varied but no limestone was added. Four runs were conducted with limestone addition (SC-1 through SC-4), and in SC-3 and SC-4 the cyclone catch was recycled to the combustor.

Brown sand was used as the bed material for the baseline tests and as the starting bed for those with limestone addition. The sand had a particle density of 2580 kg/m^3, a bulk density of 1570 kg/m^3, and a surface mean particle size of 1 mm. Its size distribution is given in Table 3.

TEST RESULTS

COMBUSTOR EQUILIBRIUM

Each test consisted of 5 to 6 h of stable operation with Syncrude coke as the only fuel. The results given in Table 4 represent the mean conditions for the last hour of each test. These can be regarded as "steady-state" conditions, except with respect to SO_2 emissions, where true equilibrium would require three or more bed turnovers, which would only be achieved in about 30 h of operation, even with the relatively shallow bed depths (500-600 mm) which were employed. However, the SO_2 emission levels after 5 to 6 h are close to equilibrium, and can be treated as a worst case.

Base-line tests indicate that 35 to 45% of the sulphur is not released as SO_2. Since the Syncrude coke contained only 6.5% ash, and the ash is low in calcium, the mechanism here is almost certainly due to elutriation of sulphur-containing solids rather than chemical capture of SO_2. Presumably tne same mechanism is in effect in the tests with limestone addition, making it difficult to assess the true relationship between Ca/S ratio and sulphur capture.

SULPHUR CAPTURE

A plot of sulphur capture versus Ca/S molar ratio corrected for an arbitrary 40% sulphur escaping the system due to elutriation (Fig. 2) suggests that sulphur capture is following an "exponential law" similar to that observed by many other workers (6), i.e.:

$$\text{sulphur capture \% } R = 100\{1 - \exp[-M(Ca/S)]\}$$

where M is an arbitary positive constant depending on experimental conditions and limestone properties. This indicates that the various sets of data obtained in this test program are consistent and meaningful even though equilibrium sulphur capture was probably not achieved. Other workers have burned Syncrude coke in very similar apparatus, and have achieved 90% sulphur capture with Ca/S ratios of 3 to 3.5 (7).

NO_x AND CO EMISSIONS

An examination of the NO_x emissions reported in Table 5 indicates that only in run SC1 are the levels above the 258 ng/J limit specified by the "national guidelines for new stationary sources" (8). Furthermore this run was carried out at a relatively high temperature of 930°C. Thus, is it clear that emission guidelines for NO_x can be achieved relatively easily. The proportion of fuel nitrogen released as NO_x is normally <10%.

The CO emissions show considerable variation. However where the flue gas oxygen is in the 4 to 6% range, levels are relatively low typically from 200 to 600 ppm. This suggests that an appropriate excess air level is 20 to 30%

COMBUSTION EFFICIENCY

Due to analytical difficulties some of the combustion efficiencies are unavailable. However, results were obtained for runs SC1 to SC4 and are reported in Table 6. The carbon losses relative to carbon input for runs in the 800°C to 850°C range are extremely high - 40 to 47%. Only in run SC1, which was carried out at 930°C, does the combustion efficiency approach more acceptable levels (74%). This agrees with other work in which combustion efficiencies above 90% were achieved at bed temperatures of about 1000°C (7). It is instructive to compare these results with those observed in CFBC tests on Syncrude coke which gave combustion efficiencies of the order of 95-99% for a similar temperature range (1,2). These results indicate clearly the limitations of BFBC when burning this particular fuel below 950°C (7).

Table 6 also demonstrates that elutriated material captured by the cyclone is by far the largest source of unburnt carbon; typically more than 90% of the total. However, a surprising result of the tests is the relatively high inventory of unburnt carbon in the bed - up to 8%. The amount of carbon passing the cyclone to the baghouse appears to be negligible instead there

seems to have been an increasing holdup of solids in the cyclone in the two tests with fly ash recycle.

This work has indicated clearly that elutriation is the primary cause of low combustion efficiencies and that fly ash recycle does not seem to have a considerable effect on combustion efficiencies over the limited range of temperatures and velocities examined. In view of the limited data, it is not advisable to draw firm conclusions about the effects of fly ash recycle on Syncrude coke combustion. However, it seems reasonable that fly ash recycle might have a more limited effect with this relatively unreactive fuel.

FLUIDIZATION CHARACTERISTICS

Run SC-1 was carried out at 0.85 m/s, using 6 mm x 0 limestone. A strong, progressive defluidization developed as shown in Fig. 3 which gives temperature-time curves for five thermocouples T2, T59, T123, T199 and T313 (where the digits refer to height above the distributor plate in mm). Subsequent runs were carried out using 1.7 mm x 0 limestone which avoided this problem. However, this clearly demonstrates that sorbent size is important when burning this fuel in a BFBC.

CONCLUSIONS

Testwork with Syncrude coke in a pilot-scale BFBC has indicated that the fine size of this material (mean size about 150 μm) demands both low fluidizing velocities (1 m/s or less) and low in-bed cooling. The low fluidizing velocities also require a careful control of sorbent size to avoid defluidization. Higher velocities cause extinction of the combustion in the bed and a massive degree of freeboard combustion which prevents control of emissions.

Combustion efficiencies were low; typically 50 to 60% at about 850°C, and 74% at 930°C. This compares unfavourably with CFBC operation which gives combustion efficiencies of 95-99% at similar temperatures and permits higher fluidizing velocities.

Without limestone injection sulphur emissions were typically in the 2500-3000 ppm range, indicating that about 40% of the fuel sulphur was not released as SO_2 but was elutriated with the unburnt carbon. Fort McMurray limestone appeared to be effective as a sulphur sorbent but qualitative

results were masked by the low combustion efficiency. NO_x emissions were well below allowable levels at about 850°C. Typically less than 10% of the fuel nitrogen was converted to NO_x.

It is very likely that acceptable combustion efficiencies could be achieved by appropriate fuel preparation such as pelletizing to reduce elutriation. It would then be possible to study the parameters affecting sulphur capture more quantitatively. However, the capability already demonstrated by circulating fluidized bed combustors to achieve good performance with Syncrude coke appears to eliminate the need for further work on bubbling fluidized bed combustors.

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Table 1 - Analysis of Syncrude coke

	Air dried (%)	Dry basis (%)
Proximate analysis		
Moisture	1.61	0.00
Ash	6.57	6.68
Volatiles	6.68	6.79
Fixed carbon (by diff)	85.14	86.53
Ultimate analysis		
Carbon	81.07	82.40
Hydrogen	1.41	1.43
Sulphur	6.85	6.96
Nitrogen	2.09	2.12
Ash	6.57	6.68
Oxygen (by diff)	0.40	0.41
Calorific Value - MJ/kg (gross)	30.01	
Btu/lb (gross)	12 910	

Table 2 - Ash analysis for Fort McMurray (Athabasca) limestone

	wt %
LOI	35.15
Ash	65.82
Ash analysis as oxide	
CO_2	33.80
CaO	41.23
SiO_2	13.56
Al_2O_3	3.31
Fe_2O_3	1.43
TiO_2	0.34
P_2O_5	0.14
MgO	0.00
SO_3	1.36
Na_2O	0.00
K_2O	1.00
BaO	0.10
SrO	0.02

Table 3 - Size distribution and composition of silica sand

Size distribution	%
>1.75 mm	5.8
1.7 x 1.2 mm	39.4
1.2 x 0.8 mm	41.6
0.8 x 0.6 mm	10.4
<0.6 mm	2.8
Analysis (wt %)	
SiO_2	99.43
Fe_2O_3	0.58
TiO_2	0.01
K_2O	0.01

Table 4 - Operating conditions for Syncrude coke and Fort McMurray limestone trials

Run No.	Coke feed rate kg/h	Limestone feed rate kg/h	Bed temp °C	Air flow m^3/h	Recycle air flow m^3/h	Fluidizing velocity m/s	CO_2 %	O_2 %	NO_x ppm	CO ppm	SO_2 IR ppm	SO_2 UV ppm
BSC1	20.58	0	841	134.9	0	0.89	14.07	3.84	250	1233	4294	4825
	[172]	<0>					(1.90)	(1.25)	(31)	(1245)	(889)	(953)
						Sulphur capture =	44.4% (IR)		or	37.5% (UV)		
BSC2	10.32	0	786	131.3	0	0.88	9.7	6.46	246	385	2554	1911
	[86]	<0>					(0.59)	(0.17)	(18)	(59)	(118)	(84)
						Sulphur capture =	35.7% (IR)		or	51.9% (UV)		
BSC3	15.49	0	841	107.0	0	0.74	16.3	4.0	472	322	4445	4568
	[129]	<0>					(0.18)	(0.11)	(21)	(63)	(65)	(38)
						Sulphur capture =	39.4% (IR)		or	37.66% (UV)		
SC1	12.92	14.08	933	112.8	0	0.85	16.25	5.30	792	469	346	552
	[108]	<3.75>					(1.12)	(1.09)	(25)	(107)	(60)	(58)
						Sulphur capture =	94.0% (IR)		or	90.5% (UV)		
SC2	16.67	22.70	843	104.7	0	0.76	19.21	2.97	776	359	259	291
	[139]	<4.68>					(0.38)	(0.08)	(23)	(113)	(15)	(8)
						Sulphur capture =	96.8% (IR)		or	96.4% (UV)		
SC3	10.65	6.32	830	99.0	11.0	0.74	18.60	2.61	552	430	1116	1230
	[89]	<2.04>					(0.16)	(0.11)	(20)	(63)	(36)	(25)
						Sulphur capture =	77.2% (IR)		or	74.9% (UV)		
SC4	20.95	6.81	826	122.0	16.0	0.93	18.87	2.55	414	1499	2389	2608
	[175]	<1.12>					(0.09)	(0.08)	(23)	(371)	(196)	(184)
						Sulphur capture =	68.9% (IR)		or	66.05% (UV)		

[ ] - refers to kW

< > - Ca/S mole ratio

( ) - Standard deviation

Table 5 - Gas emissions

Test No.	NO_x ng/J	NO_x % of fuel nitrogen	SO_2 (IR) ng/J	SO_2 (IR) % of fuel sulphur	SO_2 (UV) ng/J	SO_2 (UV) % of fuel sulphur
BSC1	69	4.3	2540	55.6	2854	62.5
BSC2	132	8.3	2933	64.3	2195	48.1
BSC3	138	8.6	2770	60.6	2847	62.34
SC1	293	18.3	273	6.0	435	9.5
SC2	206	12.9	147	3.2	165	3.6
SC3	241	15.1	1040	22.8	1146	25.1
SC4	115	7.2	1420	31.1	1550	34.0

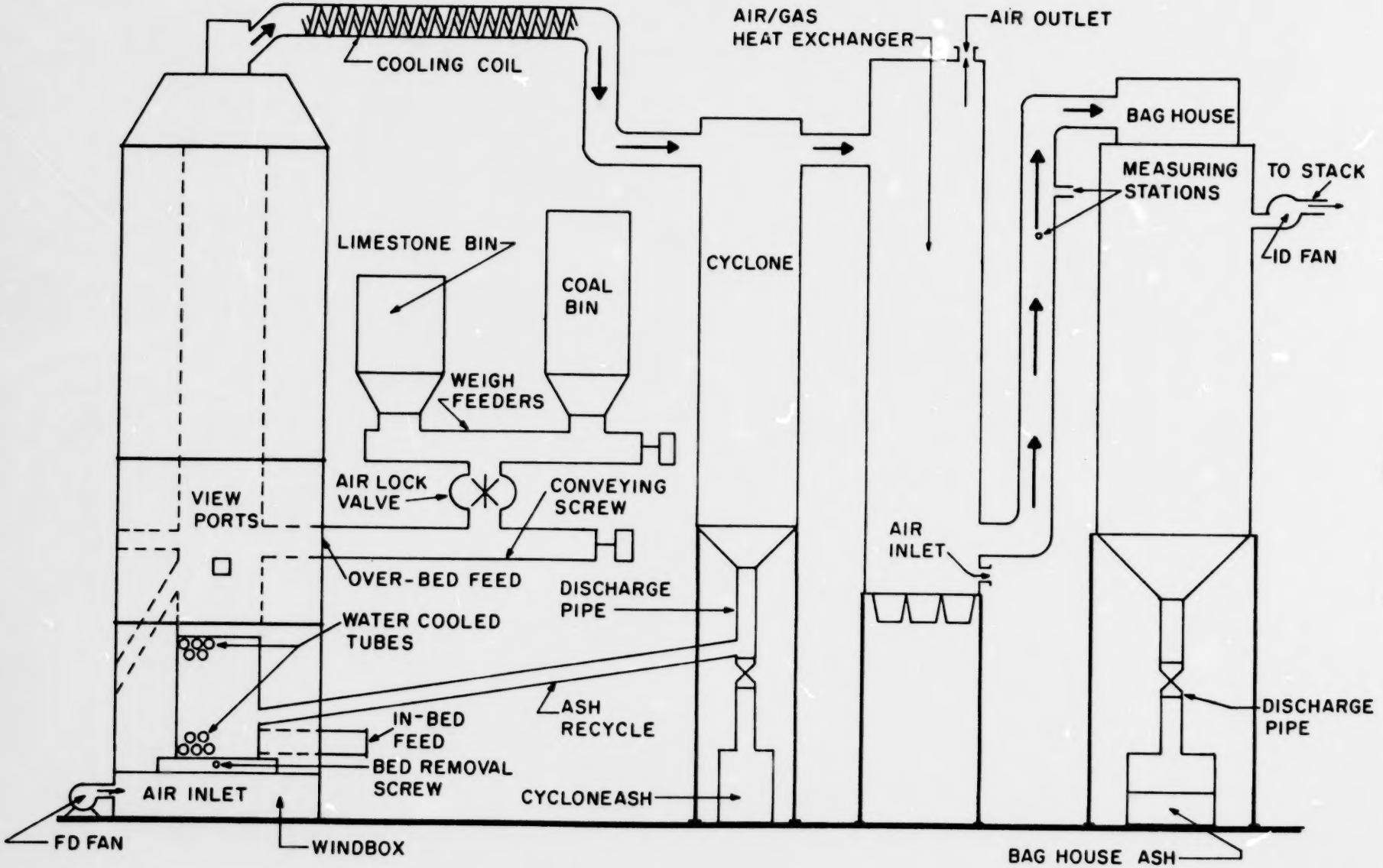
Table 6 - Combustion efficiency of carbon

Test No.	Carbon in the bed kg/h	Cyclone carbon kg/h	Fly ash carbon kg/h	Carbon combustion efficiency %
SC1	0.224 (8.3)	2.463 (91.7)	-*	74.3
SC2	0.115 (2.0)	5.572 (97.9)	0.004 (0.1)	57.9
SC3	0.078 (2.1)	3.688 (97.5)	0.017 (0.4)	56.2
SC4	0.094 (1.4)	6.809 (98.6)	-*	59.4
BSC1†	-	-	-	60
BSC2†	-	-	-	62
BSC3†	-	-	-	67

( ) - % unburnt carbon.

*Unknown, but deemed to be insignificant in combustion efficiency calculations.

†Figures based on combustion calculations thus must be regarded as tentative and are given for reason of completion only.



SCHEMATIC OF MARK II COMBUSTOR

FIG 1

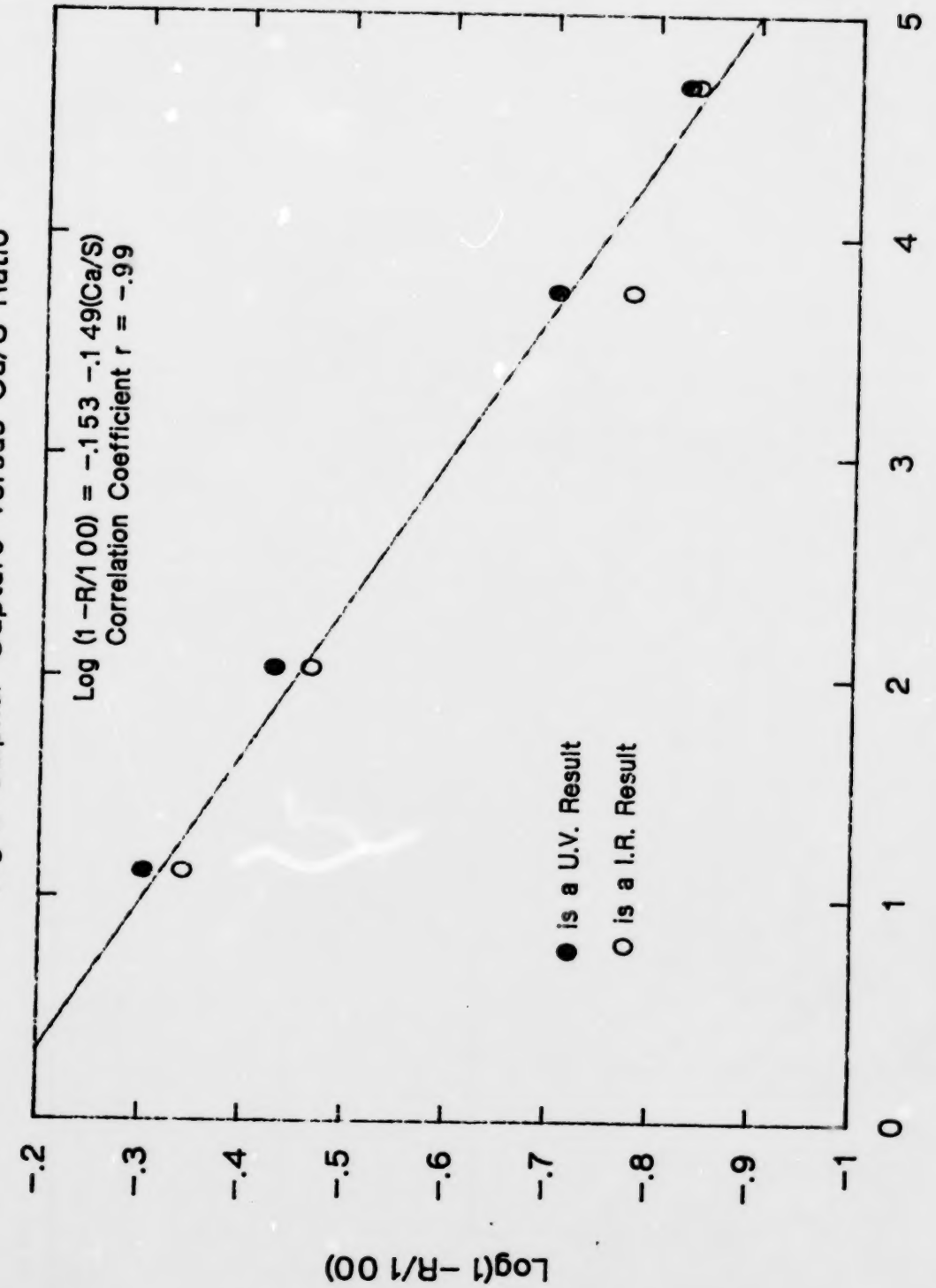


Fig 2 Sulphur Capture Versus Ca/S Ratio

Figure 3 Bed Temperature versus Time